Remarks

The Applicants acknowledge the Examiner's helpful comments concerning the IDS previously submitted. The Applicants enclose a copy of WO 93/25835, which corresponds to JP-A-7-507739. Entry into the Official File is respectfully requested. The Applicants also respectfully request that the PTO-1449 be appropriately initialed in the Official File.

The Applicants acknowledge the objection to Claims 8 and 9 under 37 C.F.R. §1.75(c). Claim 8 has been amended to remove the improper dependency. Claim 9 has been cancelled. Withdrawal of the objection is respectfully requested.

The Applicants note with appreciation the Examiner's helpful comments concerning Claim 7 and the method limitations therein. The Applicants have accordingly amended Claim 7 to recite that the layers are co-extruded layers.

The Applicants have added new Claims 10 – 25. New Claim 10 recites that the multi-layer structure does not comprise a metal layer. This is readily seen by reference to Fig. 1 and numerous of the Examples. New Claims 11 – 15 recite variations of Claims 1 and 2, which include "closed" preambles and references to the fact that the layer (a) and the layer (b) are directly in contact and bonded to each other. This is readily seen in Fig. 1 and explained in more detail in the Examples. New Claim 16 recites that the layer (a) is the outermost layer, which may also be seen in Fig. 1.

Claim 9 has been cancelled in favor of new Claims 17 and 18 that are directed to an automobile fuel pipe.

New Claim 19 recites that additional possible diamine components may be used and provides a list thereof. Support may be found on page 19 of the Specification, beginning at line 14. Claim 20 recites that the nylon 9T further comprises a terminal blocking agent. Support may be found on page

19 at line 29. Claim 21 recites that the terminal blocking agent may be monocarboxylic acid or monoamines. Support may be found in the sentence spanning pages 19 and 20.

New Claim 22 recites that the monocarboxylic acids are selected from aliphatic, alicyclic and aromatic monocarboxylic acids. Support may be found in the first full paragraph of page 20. New Claim 23 recites that the monoamines may be aliphatic, alicyclic and/or aromatic. Support may be found in the paragraph starting at line 23 of page 20.

New Claim 24 recites that the nylon 9T may further comprise other polyamide resins or thermoplastic resins. Support may be found on page 21 in the third full paragraph. Finally, new Claim 25 recites various additives that may be utilized in accordance with the nylon 9T layer. Support for those additives may be found on page 21 in the fifth full paragraph. Entry into the Official File of new Claims 10 – 25 is respectfully requested.

The Applicants acknowledge the rejections of Claims 1 – 9 under 35 U.S.C. §103 over the hypothetical combination of Oka with Katayama. The Applicants respectfully submit that the hypothetical combination is inapplicable to Claims 1 – 8 (Claim 9 having been cancelled) for the reasons set forth in detail below.

Katayama discloses a hydrogen fuel hose having a wall comprising an inner resin layer, a thin metal layer and an outer resin layer, wherein the outer resin layer may be made of PA12 and PA9T and the inner layer may be made of PA9T. However, Katayama does not disclose a multi-layer structure having a PA12 layer and a PA9T layer which are directly contacted and bonded with each other.

The subject matter of Claims 1 – 8, as described in the Specification in detail, teaches that a layer of PA11 and/or PA12 is excellent in mechanical strength, toughness, chemical resistance and flexibility and is suitable for an automobile fuel pipe. However, permeation of alcohol gasoline through the layer of PA11 and/or PA12 should be prevented. This is attained by providing a multi-layer structure comprising a layer of PA11 and/or PA12 and a layer of PA9T, which layers are directly in contact with each other. Although there have been proposed some multi-layer structures comprising a layer of PA11 and/or PA12 and a layer which prevents alcohol gasoline permeation, they have the problem of poor adhesion between the layers. In contrast, the multi-layer structure comprising a layer of PA11 and/or PA12 and a layer of PA9T of Claims 1 – 8 prevents alcohol gasoline permeation and is excellent in adhesion between the layers, which is shown in the Applicants' Examples. Thus, Claims 1 – 8 provide a multi-layer structure which is excellent in mechanical strength, toughness, chemical resistance and flexibility as well as adhesion between the layers and therefore is suitable for an automobile fuel pipe for alcohol gasoline.

Katayama is not directed to an automobile fuel pipe for alcohol gasoline and does not recognize the problem associated with the prior art automobile fuel pipes. Therefore, it would be difficult to achieve the subject matter of Claims 1 – 8 based on the teaching of Katayama.

Katayama does not teach or suggest a multi-layer structure comprising a layer of PA11 and/or PA12 and a layer of PA9T that are directly in contact. Since Katayama discloses a multi-layer structure comprising an outer resin layer, a thin metal layer and an inner resin layer, the outer and inner resin layers, even if they are PA11 or PA12 and PA9T, cannot contact each other, as in Claims 1 – 8.

Oka discloses a resin composition of PA9T, but does not disclose or suggest the problem of the conventional automobile fuel pipe and the constitution and the effect of the multi-layer structure of Claims 1 – 8 at all. Oka even does not disclose the excellent alcohol gasoline permeation prevention property of PA9T. Thus, Claims 1 – 8 are not obvious over a combination of Katayama and Oka.

Also, the Applicants note with appreciation the Examiner's frank acknowledgment that Katayama fails to disclose that the nylon 9T consists of 60 to 100 mol% of the dicarboxylic acid component being a terephthalic acid and 60 to 100 mol% of a diamine selected from 1,9-nonanediamine and 2-methyl-1,8-octanediamine. The Official Action relies on Oka to cure this deficiency of Katayama. Oka discloses a polyamide composition comprising 100 part by weight of a polyamide, from 10 to 200 parts by weight of an aromatic ring-containing bromine compound, and from 0.1 to 100 parts by weight of at least one flame-retardant synergist selected from metal salts of stannic acid and alkaline earth metal salts of boric acid. The polyamide may be any number of polyamides, including semi-aromatic polyamides comprising dicarboxylic acid units of essentially aromatic dicarboxylic acid units and diamine units of essentially aliphatic alkylenediamine units such as nylon 9T. The terephthalic acid units may be present in an amount of 60 to 100 mol% and the diamine units may be C_{6-18} aliphatic alkylenediamine units in an amount of from 60 to 100 mol%.

The problem with this disclosure is that one of ordinary skill in the art, if tempted to make the hypothetical combination with Katayama, would substitute the polyamide composition in place of the polyamides of Katayama. The essence of Oka is to have the three components, namely the polyamide, the bromine compound and the synergist. One of ordinary skill in the art would not select only the polyamide out of the three components as is demonstrated in the Examples and Comparative Examples of Oka. For example, the Applicants invite the Examiner's attention to Comparative Example 4, wherein the flame-retardant synergist has been omitted. That Comparative Example results in a poor composition. Similarly, reference to Comparative Example 5 demonstrates that, when the flame retardant is absent, poor results occur. Thus, one of ordinary skill in the art is taught by Oka to employ all of the polyamide, the bromine compound and the synergist.

However, that is not what the Applicants claims. The Applicants' layer (b) is a layer consisting essentially of a polyamide resin (nylon 9T) consisting of a bicarboxylic acid component and the diamine component with, 60 to 100 mol% of the dicarboxylic acid component being a terephthalic acid and 60 to 100 mol% of the diamine component being a diamine component selected from 1,9-nonanediamine and 2-methyl-1,8-octanediamine. In other words, the Applicants' layer (b) does not contain the bromine and does not contain the synergist that is taught by Oka. Therefore, the Applicants respectfully submit that, even if one of ordinary skill in the art were to hypothetically combine the polyamide composition of Oka with Katayama, the resulting product would still fail to teach or suggest the invention as recited in the solicited claims.

Moreover, since Oka treats nylon 9T as being essentially the equivalent of the other disclosed nylons of both Oka and Katayama, there would be no incentive for one of ordinary skill in the art to hypothetically select the nylon 9T over any other nylon in the absence of employing the bromine and the synergist. Again, the Applicants respectfully submit that the hypothetical combination fails to teach or suggest the invention as recited in the solicited claims. The Applicants therefore respectfully request withdrawal of the 35 U.S.C. §103 rejection based on Oka in combination with Katayama.

Similarly, Claims 10 to 14 are patentable over Katayama. Claim 10 recites that the multi-layer structure does not comprise a metal layer. Claim 11 recites that the multi-layer structure consists of a layer of PA11 and/or PA12 and a layer of PA9T, that is, a metal layer is excluded. Claims 12 and 13 recite that the multi-layer structure consists of resin layers, that is, a metal layer is excluded. Claims 14 and 15 recite that the multi-layer structure consists of a layer of PA11 and/or PA12 and a layer of PA9T and, optionally, a layer of PA11, PA12 or PA6, said multi-layer structure further comprising one or more thermoplastic resin layers, that is, a metal layer is excluded.

In light of the foregoing, the Applicants respectfully submit that the entire Application is now in condition for allowance, which is respectfully requested.

Respectfully submitted,

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MULTI-LAYER FUEL AND VAPOR TUBE

Patent Number:	WO9325835
Publication date:	1993-12-23
Inventor(s):	NOONE DAVID L; MITCHELL FRANK L
Applicant(s):	ITT (US)
Requested Patent:	WO9325835
Application Number:	WO1993US05531 19930610
Priority Number (s):	US19920896824 19920611; US19920897304 19920611; US19920962249 19921016
IPC Classification:	F16L9/12; F16L11/127
EC Classification:	F16L9/12G
Equivalents:	DE69326766D, DE69326766T, DE93215665U, EP0644990 (WO9325835), A1, B1, JP2812802B2, JP7507739T
Cited Documents:	DE3827092; US5076329; US5038833; US4303457; FR2114550

Abstract

A multi-layered tubing (10) for use in a motor vehicle composed of a thick outer tubing (12) having an inner and an outer face, the outer tubing made of an extrudable thermoplastic such as a polyamide; a thin intermediate bonding layer (16) bonded to the inner face of the thick outer layer, the bonding layer composed of an extrudable melt-processible thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer tubing; and an inner layer (14) bonded to the intermediate bonding layer, the inner layer composed of an extrudable, melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer. The multi-layer tubing may also include an innermost electroconductive layer and may optionally include an outer jacket.

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Description

MULTI-LAYER FUEL AND VAPOR TUBE

I. Field of the Invention:

The present invention relates to a hose for use in a motor vehicle. More particularly, the present invention relates to a multi-layer hose which can be employed as a fuel line or vapor recovery line in a motor vehicle.

II. Background of the Invention:

Single layer fuel lines and vapor return lines of synthetic materials such as polyamides have been proposed and employed in the past. Fuel lines employing such materials generally have lengths of at least several meters. It is important that the line, once installed, not materially change during the length of operation, either by shrinkage or elongation or as a result of the stresses to which the line may be subject during use.

It is also becoming increasingly important that the lines employed be essentially impervious to hydrocarbon emissions due to permeation through the tubing. It is anticipated that future Federal and state regulations will fix the limit for permissible hydrocarbon emissions due to permeation through such lines. Regulations which will be enacted in states such as California will fix the total passive hydrocarbon emission for a vehicle at 2 g/m2 per 24 hour period as calculated by evaporative emission testing methods such as those outlined in Title 13 of the California Code of Regulations, section 1976, proposed amendment of September 26, 1991. To achieve the desired total vehicle emission levels, a hydrocarbon permeation level for the lines equal to or below 0.5 g/m2 per 24 hour period would be required.

Finally, it is also imperative that the fuel line employed be impervious to interaction with corrosive materials present in the fuel such as oxidative agents and surfactants as well as additives such as ethanol and methanol.

Various types of tubing have been proposed to address these concerns. In general, the most successful of these have been co-extruded multi-layer tubing which employ a relatively thick outer layer composed of a material resistant to the exterior environment. The innermost layer is thinner and is composed of a material which is chosen for its ability to block diffusion of materials such as aliphatic hydrocarbons, alcohols and other materials present in fuel blends, to the outer layer. The materials of choice for the inner layer are polyamides such as Nylon 6, Nylon 6.6, Nylon 11, and Nylon 12.

Alcohol and aromatic compounds in the fluid conveyed through the tube diffuse at different rates through the tubing wall from the aliphatic components.

The resulting change in the composition of the liquid in the tubing can change the solubility thresholds of the material so as, for example, to be able to crystalize monomers and oligomers of materials such as Nylon 11 and Nylon 12 into the liquid. The presence of copper ions, which can be picked up from the fuel pump, accelerates this crystallization. The crystallized precipitate can block filters and fuel injectors and collect to limit travel of the fuel-pump or carburetor float as well as build up on critical control surfaces of the fuel pump.

In U.S. Patent Number 5,076,329 to Brunnhofer, a five- layer fuel line is proposed which is composed of a thick corrosion-resistant outer layer formed of a material known to be durable and resistant to environmental degradation such as Nylon 11 or Nylon 12.

The tubing disclosed in this reference also includes a thick intermediate layer composed of conventional Nylon 6. The outer and intermediate layers are bonded together by a thin intermediate bonding layer composed of a polyethylene or a polypropylene having active side chains of maleic acid anhydride. An thin inner layer of aftercondensed Nylon 6 with a low monomer content is employed as the innermost region of the tubing. The use of Nylon 6 as the material in the inner fluid contacting surface is designed to eliminate at least a portion of the monomer and oligomer dissolution which would occur with Nylon 11 or Nylon 12. The thin innermost layer is bonded to the thick intermediate layer by a solvent blocking layer formed of a copolymer of ethylene and vinyl alcohol with an ethylene content between about 30% and about 45% by weight.The use of a five layer system was mandated in order to obtain a tubing with the impact resistance of Nylon 12 with the low monomer/oligomer production of Nylon 6. It was felt that these characteristics could not be obtained in a tubing of less than five layers.

In U.S. Patent Number 5,038,833 also to Brunnhofer, a three-layer fuel line without the resistance to monomer/oligomer dissolution is proposed in which a tube is formed having a co-extruded outer wall of Nylon 11 or Nylon 12, an intermediate alcohol barrier wall formed from an ethylene-vinyl alcohol copolymer, and an inner water-blocking wall formed from a polyamide such as Nylon 11 or Nylon 12. In DE 40 06 870, a fuel line is proposed in which an intermediate solvent barrier layer is formed of unmodified Nylon 6.6 either separately or in combination with blends of polyamide elastomers. The internal layer is also composed of polyamides, preferably modified or unmodified Nylon 6. The outer layer is composed of either Nylon 6 or Nylon 12.

Another tubing designed to be resistant to alcoholic media is disclosed in UK Application Number 2 204 376 A in which a tube is produced which has an thick outer layer composed of 11 or 12 block polyamides such as Nylon 11 or Nylon 12 which may be used alone or combined with 6 carbon block polyamides such as Nylon 6 or 6.6 Nylon. The outer layer may be co-extruded with an inner layer made from alcohol-resistant polyolefin co-polymer such as a co-polymer of propylene and maleic acid. The inner layer is zinc chloride resistant Nylon 6.

Heretofore it has been extremely difficult to obtain satisfactory lamination characteristics between dissimilar polymer layers. Thus all of the multi-layer tubing proposed previously has employed polyamide-based materials in most or all of the multiple layers. While many more effective solvent-resistant chemicals exist, their use in this area is limited due to limited elongation properties, strength and compatibility with

Nylon 11 and 12.

Thus it would be desirable to provide a tubing material which could be employed in motor vehicles which would be durable and prevent or reduce permeation of organic materials therethrough. It would also be desirable to provide a tubing material which would be essentially nonreactive with components of the liquid being conveyed therein.

SUMMARY OF THE INVENTION

The present invention is a multi-layer tube which can be used on motor vehicles for applications such as in a fuel line or a vapor return or recovery line. In the first and second embodiments of the present invention, the tube is composed of:
a thick flexible outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable melt processible thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C, the melt processible thermoplastic selected from the group consisting of sixcarbon block polyamides, twelve-carbon block polyamides, eleven-carbon block polyamides,and mixtures thereof or thermoplastic elastomers commercially available under the trade names SANTOPRENE, KRATON, SARLINK, and VICHEM; ;
a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion to the outer tubing; and
an inner hydrocarbon barrier layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the thermoplastic material in the interior layer having an elongation value of at least 150% and an ability to withstand impacts of at least two ft/lbs below about -200C.

In the third embodiment of the present invention, the tube is composed of:
a thick outer tubing having a given thickness and an inner and an outer face, the outer tubing consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C;
a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt-processible thermoplastic capable of sufficiently permanent laminar adhesion to the outer layer;;
an interior layer bonded to the intermediate bonding layer, the interior layer consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the thermoplastic material containing as a major constituent, a thermoplastic which is chemically dissimilar to the thermoplastic employed in the thick outer layer, the chemically dissimilar thermoplastic being resistant to permeation and interaction with short chain aliphatic and aromatic compounds; and
an innermost electrostatic discharge integrally bonded to the multi-layer tubing, the electrostatic discharge layer consisting essentially of an extrudable, melt-processible thermoplastic material having an electrostatic dissipation capacity in a range between about 10-4 and about 10-9 ohm/cm2.

The tubing of the present invention may also include an optional outer jacket composed of a suitable melt-processible thermoplastic which is either coextruded or applied in a separate processing operation.

The thermoplastic material employed in the optional outer jacket may be any suitable material which adds insulative or cushioning properties to the tubing jacket. The outer tubing jacket may also, optionally, be capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10-4 to 10-9 ohm/cm2.

DESCRIPTION OF THE DRAWING

The objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the following drawing in which:
Fig. 1 is a sectional view through a piece of tubing of the first and second embodiments of the present invention; and
Fig. 2 is a sectional view through a piece of tubing of the third embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is a multi-layer fuel line and vapor tube which contains at least one bonding layer and at least an outer and an inner tubing layer.

The tubing of the present invention may also include at least one conductive layer. The tubing of the present invention is, preferably, fabricated by co-extruding given thermoplastic materials in a conventional coextrusion process. The tubing may either be co-extruded to a suitable length or may be co-extruded in continuous length and cut to fit the given application subsequently.

The tubing of the present invention may have an outer diameter up to 50 mm. However, in applications such as fuel lines and vapor recovery systems, outer diameter of up to 2 to 2.5 inches are preferred.

The material may have any suitable wall thickness desired. However, in automotive systems such as those described herein, wall thicknesses between 0.5 mm and 2 mm are generally employed with wall thicknesses of approximately 0.8 to 1.5 mm being preferred. While it is within the scope of this invention to prepare a tubing material having a plurality of overlaying layers of various thermoplastic materials, the tubing of the present invention generally has a maximum of five layers inclusive of the bonding layers but excluding any outer jackets. In the first and second embodiments of the present invention, the tubing material has three or four.

In the third embodiment of the present invention, the tubing material has five.

The tubing 10 of the present invention is a material which is suitable for use in motor vehicles and comprises a relatively thick outer layer 12 which is nonreactive with the external environment and can withstand various shocks, vibrational fatigue, and changes in temperature as well as exposure to various corrosive or degradative compounds to which it would be exposed through the normal course of operation of the motor vehicle.

It is anticipated that both the outer tubing layer 12 as well as any interior layers bonded thereto would be suitable for use at an outer service temperature range between about -400C and about 1500C, with a range of -200C to 1200C being preferred. The various layers of tubing are integrally laminated to one another and resistant to delamination throughout the lifetime of the tubing. The tubing of the present invention has a tensile strength of no less than 25N/mm2 and an elongation value of at least 150%. The tubing has a burst strength at 230C and 1200C of at least 20 bar. The multi-layer tubing of the present invention is sufficiently resistant to exposure to brake fluid, engine oil and peroxides such as those which may be found in gasoline.

The outer layer 12 may be composed of any meltprocessible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to environmental hazards such as zinc chloride, and degradation upon contact with engine oil and brake fluid. In general, in the first embodiment of the present invention, the outer layer 12 as depicted in
Fig. 1 consists essentially of six-carbon block polyamides, such as Nylon 6, which are resistant to degradation upon exposure to zinc chloride.In the second embodiment of the present invention as depicted in
Fig. 1 and third embodiment of the present invention as depicted in Fig. 2, the exterior layer is composed of a thermoplastic selected from the group consisting of twelve-carbon block polyamides, eleven-carbon block polyamides, zinc chloride resistant six-carbon block polyamides, and mixtures thereof as well as selected thermoplastic elastomers. The thermoplastic elastomers are proprietary compositions and commercially available under trade names such as SANTOPRENE, KRATON, SARLINK and
VICHEM.

The materials which compose the outer layers can be employed in their respective unmodified states or can be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art. In general, the respective materials which make up the outer layer 12 may be composed of any melt-processible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to environmental hazards such as zinc chloride, and degradation upon contact with engine oil and brake fluid.

In the first embodiment of the present invention, the exterior layer consists essentially of six-carbon block polyamides, such as Nylon 6, which either inherently exhibit sufficient resistance or contain effective amounts of suitable modifying agents to achieve such resistance to degradation upon exposure to zinc chloride.

The Nylon 6 which composes the outer layer can be employed can also be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art.

In the first embodiment, the outer layer 12 is, preferably composed of a polyamide thermoplastic derived from the condensation polymerization of caprolactam. Such materials are commonly referred to as six-carbon block polyamides or Nylon 6. In this embodiment, the sixcarbon block polyamide contains sufficient quantities of modifying agents to impart a level of zinc chloride resistance greater than or

equal to that required by test method SAE J844; non-reactivity after 200 hour immersion in a 50% by weight aqueous zinc chloride solution. In the preferred embodiment, the six-carbon block polyamide material is a multi-component system comprised of a
Nylon-6 copolymer blended with other Nylons and olefinic compound.The zinc-chloride resistant Nylon-6 of choice will have a melt temperature between about 2200C and 2400C. Examples of thermoplastic materials suitable for use in the tubing of the present invention are propriety materials which can be obtained commercially under the trade names M-7551 from NYCOA Corporation and ALLIED 1779 from Allied Chemical.

The six-carbon black polyamide may, optionally, include other modifying agents such as various plasticizing agents generally present in amounts between about 1.0% and about 13% by total weight of the thermoplastic composition. as are readily known in the art. The polyamide material employed, preferably, is an impact-modified material capable of withstanding impacts of at least 2 ft. lbs. at temperatures below about -200C.

In the second and third embodiments of the present invention, the outer layer 12 is composed of a thermoplastic selected from the group consisting of twelve-carbon block polyamides, eleven-carbon block polyamides as well as zinc chloride resistant six-carbon block polyamides, or thermoplastic elastomers. These thermoplastic elastomers are proprietary compositions and commercially available under trade names such as
SANTOPRENE, KRATON, SARLINK and VICHEM. The materials which compose the outer layer in the second embodiment can be present in their unmodified state or can be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art.

In the second and third embodiments, a polyamide such as Nylon 12 is, preferably, effectively employed. It is anticipated that a thermoplastic such as
Nylon 12 may be either modified or unmodified. If modified, it is anticipated that the material will contain various plasticizers as are readily known in the art. In the second embodiment, the polyamide will contain up to 17% by composition weight plasticizer; with amounts between about 1% and about 13% being preferred.

In the present invention, the outer layer 12 has a wall thickness sufficient to provide suitable strength an endurance to the multi-layer tubing of the present invention. In applications involving automotive vehicles, the outer layer 12 comprises between about 50% and about 60% of the total wall thickness. In general, in the first embodiment, the outer layer has a wall thickness between about 0.5 mm and about 0.8 mm; with a preferred wall thickness between about 0.6 mm and about 0.7 mm.

In the second embodiment, the outer layer 12, preferably, has a wall thickness between about 0.5 mm and about 1 mm with a preferred range being between about 0.6 mm and about 0.8 mm. In the third embodiment, the Nylon 12 outer layer 12 preferably has a wall thickness between about 0.5 mm and about 0.8 mm; with a preferred range between about 0.6 and about 0.75 mm. As indicated previously, the tubing material of the present invention can be extruded by conventional co-extrusion methods to any continuous length desired.

The intermediate bonding layer 14 is integrally bonded to the inner surface of the thick outer polyamide layer 12. In the first and second embodiments of the present invention, the intermediate bonding layer 14 is a chemically dissimilar permeation resistant, chemical resistant, fuel resistant thermoplastic material which is melt processible in normal ranges of extrusion, i.e.

about 1750 to about 2500C. By the term "chemically dissimilar" it is meant that the intermediate bonding layer 14 consists essentially of a non-polyamide material which is capable of adhesion to a bonding layer interposed between the thick outer layer and the inner layer in a manner which will be described subsequently.

The material employed in the intermediate bonding layer is a thermoplastic material which permits the establishment of a homogeneous bond between the inner and outer layers and exhibits properties of resistance to permeation of aliphatic and aromatic materials such as those found in fuel. The thermoplastic material employed herein is preferably a melt-processible co-extrudable thermoplastic which may or may not contain various plasticizers and other modifying agents. In general, the material employed in the intermediate bonding layer is a more elastic material than that employed in the associated inner layer.

In the first embodiment, the thermoplastic material which comprises the intermediate bonding layer 14 is a thermoplastic material selected from the group consisting of co-polymers of substituted or unsubstituted alkenes having less than four carbon atoms and vinyl alcohol, alkenes having less than four carbon atoms and vinyl acetate, and mixtures thereof. In this embodiment, the thermoplastic material employed will be resistant to permeation by and interaction with short chain aromatic and aliphatic compounds such as those which would be found in gasoline.

The preferred material employed in the first embodiment is a copolymer of ethylene and vinyl alcohol which has an ethylene content between about 27% and about 35% by weight with an ethylene content between about 27% and about 32% being preferred. Examples of suitable materials which can be employed in the tubing of the present invention include ethylene vinyl alcohol commercially available from EVA/LA.

In the first embodiment, the thermoplastic material employed in the intermediate bonding layer 14 is capable of serving as a hydrocarbon barrier to prevent significant permeation of the aromatic and aliphatic components of gasoline through to the polyamide outer layer of the tubing and thus, out to the surrounding environment. The effectiveness of the barrier layer at preventing such permeation will vary depending on numerous factors including but not limited to the thickness and composition of the inner layer, the thickness of the bonding layer and the composition of the materials conveyed through the tubing. It is anticipated that the bonding layer will be capable of providing the tubing of the present invention with a passive hydrocarbon permeation level less than about 0.5 g/m2 per 24 hour.

In the second embodiment, the thermoplastic material which comprises the interior bonding layer 16 is a thermoplastic polyester derived from ethylene glycol selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polyteremethylene terepthalate, and mixtures thereof.

The preferred material is polybutylene terepthalate.

Suitable material is commercially available under the trade name 1607 ZE40 from Hills of Dusseldorf, Germany.

In the second embodiment, the thermoplastic material employed in the intermediate bonding layer 16 also exhibits characteristics which permit resistance to permeation by short chain aromatic and aliphatic compounds. These permeation resistant characteristics synergistically interact with the inner polyamide layer such that the total permeation resistance is unexpectedly increased when the thermoplastic interior layer is bonded to the inner polyamide layer. Thus, the resistance to permeation to short chain aromatic and aliphatic hydrocarbons exhibited by the multi-layer material exceeds the permeation resistance exhibited by individual layers of either polybutylene terepthalate or polyamide of a thickness equal to or greater than the multi-ply composite of the present invention.

In the first and second embodiments, the material employed in the intermediate bonding layer 14 can, optionally, exhibit conductive characteristics rendering it is capable of dissipation of electrostatic charges in the range of 10-4 to 10-9 ohm/cm2. The thermoplastic material employed in the present invention may include, in its composition, a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof.The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the thermoplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. The amount of conductive material employed may be that amount sufficient to impart electrostatic dissipation characteristics to the tubing.

When employed, the maximum amount of conductive material in the thermoplastic material is less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith.

Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding thermoplastic material. Materials such as stainless steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

The intermediate bonding layer 14 serves to bond the thick outer layer 12 to the inner layer 16 to form a secure laminar bond therebetween. The inner layer 16 provides a stable fuel-contacting surface on the interior of the tube 10.

In the third embodiment, the tubing 10 of the present invention also includes an intermediate bonding layer 14 adhering and attached to the inner surface of the thick outer layer 12. The intermediate bonding layer 14 may be co-extruded with the other layers and is composed of a material which is capable of achieving a suitable homogeneous bond between itself, the thick outer layer and any inner layers interposed thereon. The intermediate bonding layer 14 is generally composed of a more elastic material than that employed in inner layers, the compositions of which will be described subsequently.

In the third embodiment, the intermediate bonding layer 14 is composed of a thermoplastic material which may exhibit properties of resistance to the permeation of aliphatic and aromatic materials such as those found in fuel in addition to exhibiting suitable bonding characteristics. The thermoplastic material employed herein is preferably a melt-processible coextrudable fluoroplastic blend which may optionally contain various plasticizers and other modifying agents.

The intermediate bonding layer 14 is, preferably, a blend containing polyvinylidine difluoride polymers, polyvinyl fluoride polymers, or mixtures thereof which exhibit an infinity to conventional polymers such as Nylon 12. In the preferred embodiment, polyvinylidine difluoride is employed. One such polymeric material suitable for use in the multi-layer tubing of the present invention is commercially available from Central Glass of Ube City,
Japan under the trade designation CEFRAL SOFT XUA-2.

This proprietary material is a graft copolymer of a fluorine-containing elastomeric polymer with a fluorinecontaining crystalline polymer. The elastomeric polymer is, preferably, a material copolymerized from an alkyl difluoride selected from the group consisting of vinyl difluoride, vinylidine difluoride, and mixtures thereof, and a chlorofluoroalkene selected from the group consisting of ethylene chlorotrifluoroethylene. The crystalline polymer is preferably a haloalkene such as ethylene chlorotrifluoroethylene.

In the third embodiment, the bonding layer 14 is the product of the copolymerization of ethylene chlorotrifluoroethylene and a vinylidine difluoride chlorotrifluoroethylene copolymer having a melting point between about 1800C and about 2100C and a molding temperature between about 2300C and about 2600C.

The inner layer 16 may be composed of any meltprocessible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to gasoline and its additives. The material of choice may also exhibit resistance to environmental hazards such as exposure to zinc chloride, and resistance to degradation upon contact with materials such as engine oil and brake fluid.

In the first embodiment, the preferred material is a polyamide derived from the condensation polymerization of caprolactam. Suitable materials are commonly referred to as six-carbon block polyamides or
Nylon 6. The six-carbon block polyamides employed herein may contain various plasticizers, fire retardants and the like as well as sufficient quantities of modifying agents to impart a level of zinc chloride resistance greater than or equal to that required by test method SAE J844: i.e. non-reactivity after 200 hour immersion in a 50% by weight aqueous zinc chloride solution.

In the first embodiment, the six-carbon block polyamide material employed is a multi-component system comprised of a Nylon-6 copolymer blended with other
Nylons and olefinic compounds. The six-carbon block polyamide material of choice will is preferably resistant to zinc chloride and has a melt temperature between about 2200C and 2400C. Examples of thermoplastic materials suitable for use in the tubing of the present invention are propriety materials which can be obtained commercially under the trade names M-7551 from NYCOA
Corporation and ALLIED 1779 from Allied Chemical.

In instances where the six-carbon block polyamide material employed in the first embodiment of the present invention includes plasticizing agents, these materials are generally present in amounts between about 1.0% and about 13% by total weight of the thermoplastic composition. The polyamide material employed, preferably, is an impact-modified material capable of withstanding impacts of at least 2 ft. lbs. at temperatures below about -200C.

In the first embodiment, the inner layer 16 may also contain suitable material in sufficient quantities to impart electrostatic conductivity characteristics to the tubing of the present invention. When employed, the material is preferably capable of dissipation of electrostatic charges in the range of 10-4 to 10 ohm/cm2. The thermoplastic material employed in the present invention may include, in its composition, a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof.The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the thermoplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. The amount of conductive material employed may be that amount sufficient to impart electrostatic dissipation characteristics to the tubing.

When employed, the maximum amount of conductive material in the thermoplastic material is less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith.

Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding thermoplastic material. Materials such as stainless steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

In the second embodiment, the thermoplastic material employed in the inner layer 14 is a meltprocessible extrudable thermoplastic material resistant to extreme changes in heat and exposure to chemical intervals such as are found in engine oil and brake fluid. The thermoplastic material of choice is, preferably, chemically similar in structure and composition to the thermoplastic material employed in the thick outer layer. As used herein, the term "chemically similar material" is defined as a thermoplastic material selected from the group consisting of 12 carbon block polyamides, 11 carbon block polyamides as well as zinc chloride resistant 6 carbon block polyamides, thermoplastic elastomers and mixtures thereof.The thermoplastic elastomers which can successfully be employed in the tubing of the present invention are proprietary compositions commercially available under trade names such as SANTOPRENE, KRATON, SARLINK and
VICHEM. The thermoplastic material employed in the inner layer of the tubing of the present invention either may be identical to the material employed in the thick outer layer or may be a different thermoplastic selected from those listed to take advantage of specific properties of the various thermoplastics. In the preferred embodiment, the inner layer 14 is composed of a material similar to or identical to the thick outer layer. In the preferred embodiment, a polyamide such as Nylon 12 can be effectively employed.

In the second embodiment, the thermoplastic employed in the inner layer 14 may be either modified or unmodified. If modified, it is anticipated that the material will contain various plasticizers as are readily known in the art. In the preferred embodiment, the polyamide will contain up to 17% by composition weight plasticizer; with amounts between about 1% and about 13% being preferred.

In the first embodiment, the inner layer has the minimum wall thickness sufficient to achieve the permeation resistance desired. In general, the inner layer is thinner than the outer layer with the thickness of the outer layer being between about 50% and about 60% of the total wall thickness of the tubing or between 55% and 60% of the thickness of the thick outer layer. In the specified embodiment, the inner wall thickness is between about 0.01 mm and about 0.2 mm with a thickness of about 0.05 mm to about 0.17 mm being preferred. The intermediate bonding layer generally may have a thickness less than or equal to that of the inner layer.

In the second embodiment, the inner layer 14 may have a thickness sufficient to supply strength and chemical resistance properties to the multi-layer tubing.

Specifically, the inner layer 14 is of sufficient thickness to impede permeation of aliphatic and aromatic hydrocarbon molecules and migration of those molecules through to the thick outer layer. In the present invention, the inner layer has a wall thickness less than that of the thick outer layer. In the preferred embodiment, the inner layer has a wall thickness between about 10% and 25% that of the outer layer;

preferably less than between about 0.05 mm and about 0.4 mm; with a wall thickness between about 0.1 mm and about 0.3 mm being preferred.

In the first embodiment, the intermediate bonding layer is of sufficient thickness to permit an essentially homogeneous bond between the inner and outer layers. In general, the intermediate bonding layer can be thinner than the other two layers and can constitute between about 10% and about 50% of the total wall thickness or between about 20% and about 30% of the thickness of the outer layer. In the specified embodiment, the thickness of the intermediate bonding layer is between about 0.01 mm and about 0.25 mm with a thickness between about 0.05 mm and about 0.20 mm being preferred.

In the second embodiment, the inner layer 14 and the bonding layer 16 are maintained at the minimum thickness sufficient to prevent permeation of the fuel through the tubing material to the thick outer layer and on through to the outer environment. It is preferred that the amount of hydrocarbon permeation through the tubing of the present invention be no greater than 0.5 grams per meter squared in a 24 hour interval. It is anticipated that the thickness of both the inner and intermediate layers can be modified to accomplish this end. In the preferred embodiment, the inner layer has a thickness between about 0.05 mm and about 0.2 mm with a thickness of about 0.1 mm to about 0.2 mm being preferred. The intermediate bonding layer generally has a thickness less than or equal to that of the inner layer.In general, the intermediate bonding layer has a thickness between about 0.05 mm and about 0.2 mm with a thickness between about 0.1 mm and about 0.2 mm being preferred.

In the third embodiment, the next layer is an interior layer 16 which is composed of a chemically dissimilar permeation resistant, chemical resistant, fuel resistant thermoplastic material which is meltprocessible in normal ranges of extrusion, i.e. about 1750 to about 2500C. By the term "chemically dissimilar" it is meant that the interior layer 16 is a non-polyamide material which is capable of adhesion to the interior bonding layer 14 interposed between the thick outer layer 12 and the interior layer 16.

In the preferred embodiment, the thermoplastic material which comprises the interior layer 16 is selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof. The material can also be a graft copolymer of the preceding materials together with a fluorine-containing polymer such as copolymers of vinylidine fluoride and chlorotrifluoroethane. Suitable material employed would contain between about 60% and about 80% by weight polyvinylidine difluoride. Materials so formed have a melting point between about 200 and about 2200C and a molding temperature between about 210 and about 2300C.

In the third embodiment, the multi-layer tubing of the present invention also includes an innermost electrostatic dissipation layer 18 which is also capable of serving as a hydrocarbon barrier to assist in the prevention of permeation of aromatic and aliphatic compounds found in gasoline through to the outer layer 12 of the tubing and, thus, out to the surrounding environment.

In this third embodiment, the innermost layer 18 is integrally bonded to the inner surface of the interior layer 16. In the present invention, the interior layer 18 is composed of a thermoplastic material which is chemically dissimilar to the thermoplastic material employed in the outer layer 12 which is meltprocessible in the normal ranges of extrusion, i.e. about 1750C to about 2500C. The thermoplastic material employed in the innermost layer 18 is capable of sufficiently permanent laminar adhesion to the interior layer 16.

In the third embodiment, the thermoplastic material which comprises the innermost layer 18 is selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof. The preferred material is a polyvinylidine fluoroplastic derived from the thermal dihalogenation of chlorodifluoro ethane. Suitable material is commercially available under the trade name XPV-504KRC CEFRAL SOFT CONDUCTIVE.

Alternately, the innermost layer 18 may be composed of a modified material which is chemically similar to the interior layer 16.

The innermost layer 18 exhibits electrostatic conductive characteristics in that it is capable of dissipation of electrostatic charge in the range of 10-4 to 10-9 ohm/cm2. The fluoroplastic material employed in the present invention may be inherently conductive in these ranges or, preferably, includes in its composition a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive material may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof.The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the fluoroplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. In the preferred embodiment, the fluoroplastic material contains conductive material in an amount sufficient to effect electrostatic dissipation.

However, the maximum amount employed therein is less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith.

Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding fluoroplastic material. Material such as stainless steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

In the third embodiment, the innermost layer 18 is maintained at thicknesses suitable for achieving static dissipation and suitable laminar adhesion respectively; generally between about 10% and 20% of the thick outer layer. The thickness of the innermost layer 18 is preferably between about 0.1 mm and about 0.2 mm.

The intermediate bonding layer preferably has a thickness approximately equal to the thickness of the innermost layer preferably between about 0.05 mm and about 0.15 mm.

In the third embodiment, the interior layer 16 is maintained at a thickness suitable to achieve a hydrocarbon permeation value for the tubing of the present invention no greater than about 0.5 g/m2 in a 24 hour interval. To accomplish this, the characteristics of the interior layer 16 can be relied upon solely or in concert with the intermediate bonding layer. It is anticipated that the thickness of the inner and intermediate layers can be modified to accomplish this end. In this embodiment, the interior layer 16 has a thickness between about 10% and about 20% of the thick outer layer. The interior layer has a thickness between about 0.15 mm and about 0.25 mm with a thickness of about 0.18 mm to about 0.22 mm being preferred. The intermediate bonding layer 14 is maintained at a thickness sufficient to permit sufficient laminar adhesion between the outer and interior layers.The intermediate bonding layer generally has a thickness less than that of the inner layer 16. The thickness of this layer is, preferably, between about 0.05 and about 0.1 mm.

The total wall thickness of the tubing of the present invention is generally between about 0.5 mm and about 2.0 mm with a wall thickness between about 0.8 and about 1.25 mm being preferred.

The tubing of the present invention may also, optionally include an outer jacket (not shown) which surrounds the outer layer. The fourth outer jacket may be either co-extruded with the other layers during the extrusion process or may be put on in a subsequent process such as cross-extrusion. The outer jacket may be made of any material chosen for its structural or insulative characteristics and may be of any suitable wall thickness. Preferably, the outer jacket may be made of a thermoplastic material selected from the group consisting of zinc-chloride resistant Nylon 6, Nylon 11, Nylon 12, polypropylene, and thermoplastic elastomers such as SANTOPRENE, KRATON, VICHEM and SARLINK. If desired, these materials may be modified to include flame retardants, plasticizers and the like.

In the second embodiment, the outer jacket may, preferably, exhibit conductive characteristics in that it is capable of dissipation of electrostatic charge in the range of 10-4 to 10-9 ohm/cm2. The material which composes the outer jacket may be inherently conductive in these ranges or, preferably, includes in its composition a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof. The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the outer jacket is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. In the preferred embodiment, the thermoplastic material contains conductive material in an amount sufficient to effect electrostatic dissipation.

However, the maximum amount employed therein is preferably less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith.

Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding thermoplastic material. Material such as stainless steel are more likely to be interstitially integrated into the 8crystalline structure of the polymer.

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Claims

What is claimed is:

1. A layered tubing for use in a motor vehicle, the tubing comprising:
a thick flexible outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C, wherein the extrudable thermoplastic of the thick outer tubing is a melt-processible thermoplastic selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof;;
a thin intermediate bonding layer bonded to the inner face of the thick outer tubing, the bonding layer consisting essentially of an extrudable melt processible thermoplastic resistant to permeation by short-chain hydrocarbons, the bonding layer consisting of a thermoplastic which is chemically dissimilar to the extrudable thermoplastic employed in the outer tubing and is capable of sufficiently permanent laminar adhesion to the inner face of the thick outer tubing; and
an inner layer having a thickness less than the thickness of the outer tubing bonded to the intermediate bonding layer, the inner layer consisting of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C.

2. The tubing of claim 1 wherein the outer layer is composed of a thermoplastic consisting essentially of an extrudable thermoplastic six-carbon block polyamide.

3. The tubing of claim 2 wherein the inner layer functions as a hydrocarbon barrier layer and is composed of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the inner layer consisting essentially of an extrudable thermoplastic six-carbon block polyamide.

4. The tubing of claim 3 wherein the inner layer is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10-4 to 10-9 ohm/cm2.

5. The tubing of claim 3 wherein the inner hydrocarbon layer contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10-4 to 10-9 ohm/cm2.

6. The tubing of claim 5 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

7. The tubing of claim 6 wherein the conductive material is present in an amount less than about 5% by volume of the polymeric material.

8. The tubing of claim 2 wherein the extrudable thermoplastic polyamide of the thick outer layer is a derived by the condensation polymerization of caprolactam.

9. The tubing of claim 8 wherein the extrudable thermoplastic polyamide of the thick outer layer consists essentially of Nylon 6 and additive materials present in sufficient quantities to impart resistance

to exposure to zinc chloride.

10. The tubing of claim 8 wherein the thick outer layer is essentially non-reactive after 200 hour immersion in a 50% by weight aqueous zinc chloride solution.

11. The tubing of claim 3 wherein the thermoplastic material employed in the intermediate bonding layer exhibits at least some resistance to interaction with short-chain hydrocarbon molecules present in material conveyed through the tubing.

12. The tubing of claim 11 wherein the thermoplastic material employed in the intermediate bonding layer includes as a major constituent an extrudable, melt processible thermoplastic selected from the group consisting of co-polymers of alkenes having less than four carbon atoms and vinyl alcohol, copolymers of alkenes having less than four carbon atoms and vinyl acetate, and mixtures thereof.

13. The tubing of claim 1 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

14. The tubing of claim 1 wherein the extrudable thermoplastic of the thick outer tubing is a melt-processible thermoplastic selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant
Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

15. The tubing of claim 14 wherein the outer tubing comprises:
an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, and mixtures thereof; and
between about 1 and about 17% by volume of a thermoplastic plasticizer material.

16. The tubing of claim 15 wherein the outer layer is composed of Nylon 12.

17. The tubing of claim 16 wherein the thermoplastic material employed in the intermediate bonding layer exhibits at least some resistance to interaction with short-chain hydrocarbon molecules present in material conveyed through the tubing.

18. The tubing of claim 17 wherein the thermoplastic material employed in the intermediate bonding layer includes as a major constituent an extrudable, melt processible thermoplastic is a thermoplastic polyester selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polyteremethylene terepthalate, and mixtures thereof.

19. The tubing of claim 18 wherein the thermoplastic material employed in the intermediate bonding layer consists essentially of polybutylene terepthalate.

20. The tubing of claim 18 wherein the extrudable melt-processible thermoplastic of the inner layer is selected from the group consisting of Nylon 11,
Nylon 12, zinc chloride-resistant Nylon 6, and mixtures thereof.

21. The tubing of claim 20 wherein the inner tubing comprises:
an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, Nylon 6, and mixtures thereof; and
between about 1 and about 17% by volume of a thermoplastic plasticizer material.

22. The tubing of claim 14 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, and mixtures thereof.

23. The tubing of claim 22 wherein said outer jacket is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10-4 to 10-9 ohm/cm2.

24. The tubing of claim 22 wherein the outer jacket contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10-4 to 10-9 ohm/cm2.

25. The tubing of claim 24 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

26. A layered tubing for use in a motor vehicle, the tubing being resistant to hydrocarbon emissions, the tubing comprising:
an outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable melt processible six-carbon block polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C, the six-carbon block polyamide being essentially non-reactive with zinc chloride;
an intermediate bonding layer having a thickness between about 0.01 mm and about 0.2 mm bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer tubing and exhibiting at least some resistance to short-chain hydrocarbon molecules conveyed through the tubing; and
an inner layer bonded to the intermediate bonding layer having a thickness between about 0.01 mm and about 0.2 mm, the inner layer consisting essentially of an extrudable, melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the inner layer consisting essentially of an extrudable thermoplastic six-carbon block polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C.

27. The tubing of claim 26 wherein the reduced hydrocarbon emission rate is less than about 0.5g/m2 per 24 hour interval.

28. The tubing of claim 26 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, polypropylene and mixtures thereof.

29. A layered tubing for use in a motor vehicle, the tubing comprising:
an outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C, wherein the outer tubing comprises:
a) an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, Nylon 6, and mixtures thereof; and
b) between about 1 and about 17% by volume of a thermoplastic plasticizer material;
an intermediate bonding layer having a thickness between about 0.05 mm and about 0.2 mm bonded to the inner face of the thick outer tubing, the bonding layer consisting essentially of an extrudable nonpolyamide thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer tubing and exhibiting at least some resistance to short-chain hydrocarbon molecules conveyed through the tubing, wherein the extrudable thermoplastic of the intermediate bonding layer is a thermoplastic polyester selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polymethylene terepthalate, and mixtures thereof; and
an inner layer bonded to the intermediate bonding layer having a thickness between about 0.05 mm and about 0.2 mm, the inner layer consisting essentially of an extrudable, melt processible polyamide capable of sufficiently permanent laminar adhesion with the intermediate bonding layer selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant
Nylon 6, and mixtures thereof.

30. The tubing of claim 29 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, polypropylene and mixtures thereof.

31. The tubing of claim 30 wherein said outer jacket is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10-4 to 10-9 ohm/cm2.

32. A layered tubing for use in a motor vehicle, the tubing comprising:
a thick flexible outer tubing having a given thickness and an inner and an outer face, the outer tubing consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C;
an intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion to the inner face of the outer tubing;;
an interior layer bonded to the intermediate bonding layer, the interior layer consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the melt-processible thermoplastic which is chemically dissimilar to

the thermoplastic employed in the thick outer layer, the chemically dissimilar thermoplastic being resistant to permeation by and interaction with short-chain aliphatic and aromatic hydrocarbon compounds; and
an innermost electrostatic dissipation layer integrally bonded to the multi-layer tubing, the electrostatic dissipation layer consisting of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer and of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10-4 to 10-9 ohm/cm2.

33. The multi-layer tubing of claim 32 wherein the interior layer is a thermoplastic material consisting essentially of a fluoroplastic material selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof.

34. The multi-layer tubing of claim 33 wherein the fluoroplastic material further consists of copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof.

35. The multi-layer tubing of claim 34 wherein the interior layer has a thickness between about 10% and about 20% of the thick outer layer.

36. The multi-layer tubing of claim 35 wherein the innermost electrostatic discharge layer consists of a thermoplastic material which is chemically dissimilar to the thick outer layer.

37. The multi-layer tubing of claim 36 wherein the innermost electrostatic discharge layer consists essentially of a thermoplastic material which consists essentially of a fluoroplastic selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof.

38. The multi-layer tubing of claim 37 wherein the fluoroplastic material further comprises copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof.

39. The multi-layer tubing of claim 38 wherein the innermost electrostatic barrier layer has a thickness between about 0.1% and about 0.2t of the thick outer layer.

40. The multi-layer tubing of claim 39 wherein the innermost electrostatic dissipation layer contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10-4 to 10-9 ohm/cm2.

41. The tubing of claim 40 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

42. The tubing of claim 41 wherein the conductive material is present in an amount less than about 5% by volume of the polymeric material.

43. The multi-layer tubing of claim 42 wherein the bonding layer is a thermoplastic material consisting essentially of:
a fluoroplastic material selected from the group consisting of ethylene dichlorotrifluoroethylene, and mixtures thereof; and
a graft copolymer selected from the group consisting of copolymers of vinylidine difluoride and chlorotrifluoroethylene copolymerized with polyvinylidine difluoride, copolymers of vinylidine difluoride and chlorotrifluoroethylene copolymerized with ethylene dichlorotrifluoroethylene, and mixtures thereof.

44. The tubing of claim 43 wherein the conductive material is elemental carbon and is copolymerized with the extrudable fluoroplastic material.

45. The tubing of claim 32 wherein the extrudable thermoplastic of the thick outer tubing is a polyamide selected from the group consisting of Nylon 11,
Nylon 12, zinc chloride resistant Nylon 6, Santoprene,
Kraton, Vichem, Sarlink and mixtures thereof.

46. The tubing of claim 32 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton,

Vichem, Sarlink and mixtures thereof.

47. A layered tubing for use in a motor vehicle, the tubing comprising:
a thick flexible outer tubing having a given thickness and an inner and an outer face, the outer tubing consisting essentially of an extrudable polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -200C;
an intermediate bonding layer having a thickness between about 0.05 mm and about 0.1 mm bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer tubing;;
an interior layer bonded to the intermediate bonding layer, the interior layer having a thickness between about 0.05 mm and about 0.15 mm and consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the melt-processible thermoplastic resistant to permeation by and interaction with short-chain aliphatic and aromatic hydrocarbon compounds selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof; and
an innermost electrostatic dissipation layer integrally bonded to the multi-layer tubing, the electrostatic discharge layer having a thickness between about 0.1 mm and about 0.2 mm and consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer and of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10-4 to 10-9 ohm/cm2, the innermost electrostatic dissipation layer selected from the group consisting of a fluoroplastic selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, wherein the thermoplastic material of the innermost hydrocarbon barrier layer is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10-4 to 10-9 ohm/cm2.

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